Chemistry 163B Winter 2013
notes for Carnot Arithmetic and Efficiency

Chemistry 163B

Carnot Arithmetic

Challenged Penmanship

Notes

see handout: Carnot Arithmetic

1

roadmap for second law

1. Phenomenological statements (what is ALWAYS observed)
2. Ideal gas Carnot *[reversible]* cycle efficiency of heat → work (Carnot cycle transfers heat only at T_U and T_L)
3. Any cyclic engine operating between T_U and T_L must have an equal or lower efficiency than Carnot OR VIOLATE one of the phenomenological statements (observations)
4. Generalize Carnot to any reversible cycle (E&R fig 5.4)
5. Show that for this REVERSIBLE cycle

   $q_U + q_L \neq 0$ ($đq$ *inexact differential)*

   but

   $\frac{q_U}{T_U} + \frac{q_L}{T_L} = 0$ (*something special about* $\frac{đq_{rev}}{T}$)
6. S, entropy and spontaneous changes

2

from lecture on 2nd Law and probability (disorder)

(*something special about* $\frac{đq_{rev}}{T}$)

- Disorder, **W**, did not change during an adiabatic reversible expansion (q_{rev} =0)
- Disorder, **W**, increased in isothermal reversible expansion (q_{rev} >0)
- Disorder, **W**, increased with T increase (q>0)
- Disorder, **W**, decreased with T decrease (q<0)
- As T → 0, **W** →1

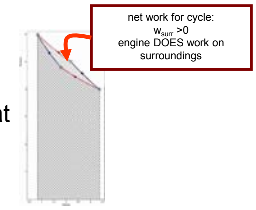
3

statements of the Second Law of Thermodynamics (roadmap #1)

1. Macroscopic properties of an isolated system eventually assume constant values (e.g. pressure in two bulbs of gas becomes constant; two block of metal reach same T) [*Andrews. p37]*
2. It is impossible to construct a device that operates in cycles and that converts heat into work without producing some other change in the surroundings. *Kelvin's Statement [Raff p 157]; Carnot Cycle*
3. It is impossible to have a natural process which produces no other effect than absorption of heat from a colder body and discharge of heat to a warmer body. *Clausius's Statement, refrigerator*
4. In the neighborhood of any prescribed initial state there are states which cannot be reached by any adiabatic process
~ *Caratheodory's statement [Andrews p. 58]*

4

goals of Carnot arithmetic (step 2 of roadmap)



1. Carnot cycle is "engine" that produces work from heat
2. Define efficiency:
   efficiency=(net work done by machine)/(heat energy input to machine)
3. Today, arithmetic manipulations of 1st Law results from ideal gas Carnot cycle (HW2 #10) to show that this efficiency depends only on the two temperatures at which heat is transferred to and from surroundings (the T_U of step 1 and T_L of step 3; the non-adiabatic paths)

5

from Carnot cycle

for system in complete cycle:
$\Delta U=0$; $q>0$; $w<0$ (work DONE on surr) **(#10E)**

$q > 0$ (q_{in}) at higher T_H; $q < 0$ (q_{out}) at lower T_L

efficiency= $-w/q_{1\to 2}$
(how much net **work out** (-sign) for **heat in** $1\to 2$)

efficiency will depend on T_U and T_L

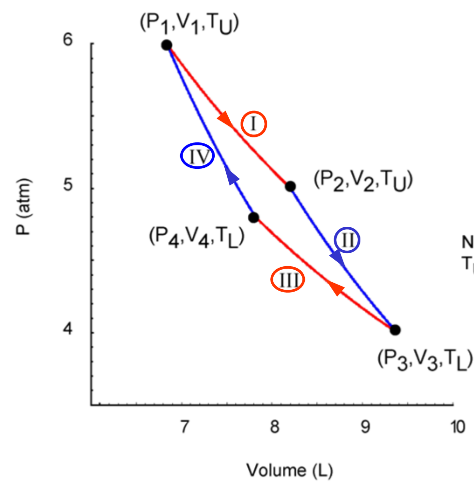
HW4 prob #22 ε is εfficiency

$$\varepsilon = \frac{T_H - T_C}{T_H} \quad or \quad \varepsilon = \frac{T_U - T_L}{T_U}$$

H=HOT C=COLD or U=UPPER L=LOWER

6

Problem HW2 #10 (see handout "Carnot Cycle Arithmetic)



P_1=6 atm, T_1=T_U=500K

P_2=5 atm, T_2=T_U=500K

P_3=4 atm, $q_{2\rightarrow3}$ = 0, T_3=T_L

P_4=4.8 atm, T_4=T_L, $q_{4\rightarrow1}$= 0

NOTE:
T_U (T *upper*) ≡T_H (T *higher* or T *hotter*)

cyclic process

I isothermal expansion
II adiabatic expansion
III isothermal compression
IV adiabatic compression

7

let's go

- get $w_I + w_{II} + w_{III} + w_{IV} = w_{total}$

- get $q_I = q_{input}$

8

Summary

(see handout "Summary of Heat and Work for the Carnot Cycle Engines, Refrigerators, Heat Pumps")

ENGINE	q	w_{sys}	w_{surr}	
I. isothermal expansion	$+nRT_U \ln\frac{P_1}{P_2}$ 1.3	$-nRT_U \ln\frac{P_1}{P_2}$ 1.2	$+nRT_U \ln\frac{P_1}{P_2}$	heat in at T_H work out
II adiabatic expansion	0	$n\overline{C}_V(T_L - T_U)$ 2.4	$-n\overline{C}_V(T_L - T_U)$	work out
III. isothermal compression	$nRT_L \ln\frac{P_3}{P_4} = -nRT_L \ln\frac{P_1}{P_2}$ 3.3&T.3	$-nRT_L \ln\frac{P_3}{P_4} = nRT_L \ln\frac{P_1}{P_2}$ 3.2&T.3	$-nRT_L \ln\frac{P_1}{P_2}$	heat lost at T_L work in
IV. adiabatic compression	0	$n\overline{C}_V(T_U - T_L)$ 4.4	$-n\overline{C}_V(T_U - T_L)$	work in
net gain/cost	$q_{in} = q_I$ $+nRT_U \ln\frac{P_1}{P_2}$		$w_{total}= w_I+w_{II}+w_{III}+w_{IV}=$ $nR(T_U - T_L)\ln\frac{P_1}{P_2}$	$\varepsilon=w_{surr}/q_{in}$ $\varepsilon= (T_U-T_L)/T_U$

9

isothermal expansion at T_U (see handout "Carnot Cycle Arithmetic)

Step I Isothermal expansion, T_U, $V_1 \rightarrow V_2$:

$$\Delta U_I = 0 \quad (1.1)$$

$$w_I = -nRT_U \ln\frac{V_2}{V_1} = nRT_U \ln\frac{P_2}{P_1} \quad (1.2)$$

$$q_I = -w_I = nRT_U \ln\frac{V_2}{V_1} = nRT_U \ln\frac{P_1}{P_2} \quad (1.3)$$

10

step II: adiabatic reversible compression $T_U \longrightarrow T_L$

$$V_3 = V_2\left(\frac{T_U}{T_L}\right)^{\frac{\overline{C_V}}{R}} \qquad V_3 = V_2\left(\frac{P_2}{P_3}\right)^{\frac{\overline{C_V}}{\overline{C_P}}} \qquad (2.1)$$

$$T_L = T_U\left(\frac{V_2}{V_3}\right)^{\frac{R}{\overline{C_V}}} \qquad T_L = T_U\left(\frac{P_3}{P_2}\right)^{\frac{R}{\overline{C_P}}} \qquad (2.2)$$

$$P_3 = P_2\left(\frac{V_3}{V_2}\right)^{\frac{\overline{C_P}}{\overline{C_V}}} \qquad P_3 = P_2\left(\frac{T_L}{T_U}\right)^{\frac{\overline{C_P}}{R}} \qquad (2.3)$$

P,V,T relationships for adiabatic reversible process

$$q_{II} = 0; \qquad w_{II} = \Delta U \qquad (2.4)$$

$$\Delta U_{II} = n\overline{C_V}\Delta T = n\overline{C_V}(T_L - T_U)$$

$$\Delta U_{II} = n\overline{C_V}T_U\left(\left(\frac{V_2}{V_3}\right)^{\frac{R}{\overline{C_V}}} - 1\right) = n\overline{C_V}T_U\left(\left(\frac{P_3}{P_2}\right)^{\frac{R}{\overline{C_P}}} - 1\right) \qquad (2.5)$$

11

Step III: isothermal reversible compression at T_L

$$\Delta U_{III} = 0 \qquad (3.1)$$

$$w_{III} = -nRT_L \ln\frac{V_4}{V_3} = nRT_L \ln\frac{P_4}{P_3} \qquad (3.2)$$

$$q_{III} = -w_{III} = nRT_L \ln\frac{V_4}{V_3} = nRT_L \ln\frac{P_3}{P_4} \qquad (3.3)$$

12

Step IV: adiabatic reversible compression ($T_L \longrightarrow T_U$)

$$V_4 = V_1\left(\frac{T_U}{T_L}\right)^{\frac{\overline{C_V}}{R}} \qquad V_4 = V_1\left(\frac{P_1}{P_4}\right)^{\frac{\overline{C_V}}{\overline{C_P}}} \qquad (4.1)$$

$$T_L = T_U\left(\frac{V_1}{V_4}\right)^{\frac{R}{\overline{C_V}}} \qquad T_L = T_U\left(\frac{P_4}{P_1}\right)^{\frac{R}{\overline{C_P}}} \qquad (4.2)$$

$$P_4 = P_1\left(\frac{V_1}{V_4}\right)^{\frac{\overline{C_P}}{\overline{C_V}}} \qquad P_4 = P_1\left(\frac{T_L}{T_U}\right)^{\frac{\overline{C_P}}{R}} \qquad (4.3)$$

P,V,T relationships for adiabatic reversible process

$$q_{IV} = 0; \qquad w_{IV} = \Delta U_{IV} \qquad (4.4)$$

$$\Delta U_{IV} = n\overline{C_V}\Delta T = n\overline{C_V}(T_U - T_L)$$

$$\Delta U_{IV} = n\overline{C_V}T_U\left(1-\left(\frac{V_1}{V_4}\right)^{\frac{R}{\overline{C_V}}}\right) = n\overline{C_V}T_U\left(1-\left(\frac{P_4}{P_1}\right)^{\frac{R}{\overline{C_P}}}\right) \qquad (4.5)$$

13

and now for the TOTAL cycle (T_U and T_L; and P_1 and P_2 given)

$w_{total} = w_I + w_{II} + w_{III} + w_{IV}$

$w_{II} = -w_{IV} \Longrightarrow w_{total} = w_I + w_{III}$

$$w_I = nRT_U \ln\frac{P_2}{P_1}$$

$$w_{III} = nRT_L \ln\frac{P_4}{P_3} \quad \textit{with} \quad P_3 = P_2\left(\frac{T_L}{T_U}\right)^{\frac{\bar{C}_P}{R}} \quad \textit{and} \quad P_4 = P_1\left(\frac{T_L}{T_U}\right)^{\frac{\bar{C}_P}{R}}$$

$$w_{III} = nRT_L \ln\left(\frac{P_1\left(\frac{T_L}{T_U}\right)^{\frac{\bar{C}_P}{R}}}{P_2\left(\frac{T_L}{T_U}\right)^{\frac{\bar{C}_P}{R}}}\right) = nRT_L \ln\left(\frac{P_1}{P_2}\right)$$

$$w_{total} = nR\left(T_U - T_L\right)\ln\frac{P_2}{P_1}$$

14

and NOW EFFICIENCY ε

efficiency: $\varepsilon = \dfrac{\text{(total work done ON SURROUNDINGS)}}{\text{(heat INPUT)}}$

only q_I
q_{III} is wasted heat lost to surroundings as thermal pollution

$$\varepsilon = \frac{-w_{total}}{q_I}$$

$$w_{total} = nR(T_U - T_L)\ln\frac{P_2}{P_1}$$

$$q_I = -w_I = nRT_U \ln\frac{P_1}{P_2}$$

and

$$\varepsilon = \frac{-nR(T_U - T_L)\ln\frac{P_2}{P_1}}{nRT_U \ln\frac{P_1}{P_2}}$$

$$\varepsilon = \frac{(T_U - T_L)}{T_U} = 1 - \frac{T_L}{T_U}$$

15

Summary

(see handout "Summary of Heat and Work for the Carnot Cycle Engines, Refrigerators, Heat Pumps")

ENGINE	q	w_{sys}	w_{surr}	
I. isothermal expansion	$+nRT_U \ln\frac{P_1}{P_2}$ 1.3	$-nRT_U \ln\frac{P_1}{P_2}$ 1.2	$+nRT_U \ln\frac{P_1}{P_2}$	heat in at T_H work out
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IV. adiabatic compression	0	$n\overline{C}_V(T_U - T_L)$ 4.4	$-n\overline{C}_V(T_U - T_L)$	work in
net gain/cost	$q_{in} = q_I$ $+nRT_U \ln\frac{P_1}{P_2}$		$w_{total} = w_I + w_{II} + w_{III} + w_{IV} =$ $nR(T_U - T_L)\ln\frac{P_1}{P_2}$	$\varepsilon = w_{surr}/q_{in}$ $\varepsilon = (T_U - T_L)/T_U$

16

some limits on efficiency of ideal engine

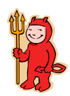
$$\varepsilon = \frac{(T_U - T_L)}{T_U} = 1 - \frac{T_L}{T_U}$$

$$\lim_{T_L \to T_U} \varepsilon = 0$$

must have q in at higher and q out at lower T

$$\lim_{T_L \to 0} \varepsilon =$$

or **1**



$$\lim_{T_U \to \infty} \varepsilon =$$

perfect efficiency at finite temperatures only for $T_{LOWER} = 0$ K

17

take home messages (lecture 8) and statements of 2nd Law (Andrews)

Two bodies 500 molecules each
one at $T_A = .63 \times T_f$,
the other at $T_B = 1.37 \times T_f$

.63 T_f	1.37 T_f

~ microstates

$\approx 10^{556} = 10^{202} \times 10^{354}$

(relative)
ORDER

bring into thermal contact

STAY COLD-HOT ??

spontaneous

or

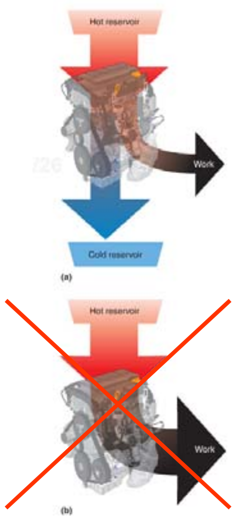
EQUILIBRIUM ??

$T_E = T_f$

(relative)
DISORDER
$\approx 10^{594}$

18

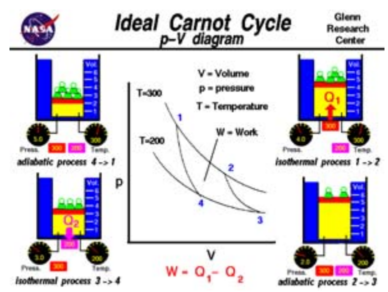
E&R fig 5.3, p. 89



These considerations on the efficiency of reversible heat engines led to the Kelvin–Planck formulation of the **second law of thermodynamics:**

> It is impossible for a system to undergo a cyclic process whose sole effects are the flow of heat into the system from a heat reservoir and the performance of an equal amount of work by the system on the surroundings.

FIGURE 5.3
(a) A schematic model of the heat engine operating in a reversible Carnot cycle. The relative widths of the two paths leaving the hot reservoir show the partitioning between work and heat injected into the cold reservoir. **(b)** The second law of thermodynamics asserts that it is impossible to construct a heat engine that operates using a single heat reservoir and converts the heat withdrawn from the reservoir into work with 100% efficiency as shown.



19

take home messages (lecture 8) and statements of 2nd Law (Clausius)

Two bodies 500 molecules each
one at T_A=.63 × T_f,
the other at T_B=1.37 × T_f

.63 T_f	1.37 T_f

~ microstates

≈10^{556}=
10^{202}×10^{354}
(relative)
ORDER

(keep) transferring heat from warm side to cold side

will not occur spontaneously (requires work a la refrigerator)

T_E= T_f

(relative)
DISORDER
≈10^{594}

20

End of Lecture 9

21